

Impurity Cation Diffusion in Perovskite-type Oxide, YCrO_3

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Introduction

The perovskite-type oxides have been widely used as component materials of a solid state electrochemical device like a solid oxide fuel cell. The oxides are often supposed to serve under various thermodynamic forces for a long time at elevated temperature. In a long-term operation, thus, an appreciable cation transport may occur, resulting in an undesirable phenomenon such as a chemical reaction between oxides and kinetic demixing. The cation transport is deeply related to defect structure of the oxide. For the perovskite system, however, little is known for its defect structure especially on cationic sub-lattices.

This work is aimed to investigate the defect structure on cation sub-lattice of a perovskite-type oxide. To this end, the diffusion coefficients of impurity cations were measured as a function of temperature and oxygen partial pressure by constructing a diffusion couple of ABO_3 and lightly doped ABO_3 , $(\text{AA}')\text{BO}_3$ or $\text{A}(\text{BB}')\text{O}_3$. In the present work, YCrO_3 was chosen as a model oxide, and La and Mn were chosen as impurities for A- and B-site diffusion experiments, respectively.

Experimental

The powder of pure and doped YCrO_3 was prepared via a citrate process and sintered by hot-press at 1500°C under a uni-axial pressure of 16MPa for 3min. The relative density of the sintered body was over 95%. To make the diffusion couple, the specimen of YCrO_3 measuring $4 \times 4 \times 0.5 \text{ mm}^3$ was first annealed at a prefixed thermodynamic condition for 1 day, and, subsequently, a thin film of doped YCrO_3 , $(\text{La}_{0.01}\text{Y}_{0.99})\text{CrO}_3$ or $\text{Y}(\text{Cr}_{0.99}\text{Mn}_{0.01})\text{O}_3$ was deposited on the polished surface by a laser ablation method. The film thickness was 400–500nm. The diffusion couple was, then, annealed for 24–360h depending on thermodynamic condition. The depth profiles of La and Mn were measured by secondary ion mass spectroscopy using Cs^+ as a primary ion. After SIMS analysis, the analyzed depth was measured using a surface profiler.

Results and discussion

Fig. 1 shows a typical depth profile as measured. Assuming that, within a doping range, the intensity of secondary ion is proportional to concentration, the raw data were converted to the normalized concentration as a function of a depth from the surface. The impurity diffusion coefficients, D_{La} or D_{Mn} were determined by fitting a diffusion profile to an infinite source solution with the assumption that the diffusion coefficient is a constant within a doping range.

Fig. 2 shows the impurity diffusion coefficients, D_{La} and D_{Mn} against the oxygen partial pressure, P_{O_2} at 1000°C . The diffusivities of both La and Mn impurity ion were in the range of $10^{-17} \sim 10^{-18} \text{ cm}^2/\text{sec}$ within experimental range. It is noted that the diffusivity of B-site impurity ion was comparable with that of A-site impurity ion. Both D_{La} and D_{Mn} show similar dependence on P_{O_2} , that is, decrease with decreasing P_{O_2} . This indicates that a simple

Schottky-type defect model ($0 = \text{V}_\text{A}^{\text{III}} + \text{V}_\text{B}^{\text{III}} + 3\text{V}_\text{O}^{\text{II}}$) may be assumed to establish the defect diagram of YCrO_3 system.

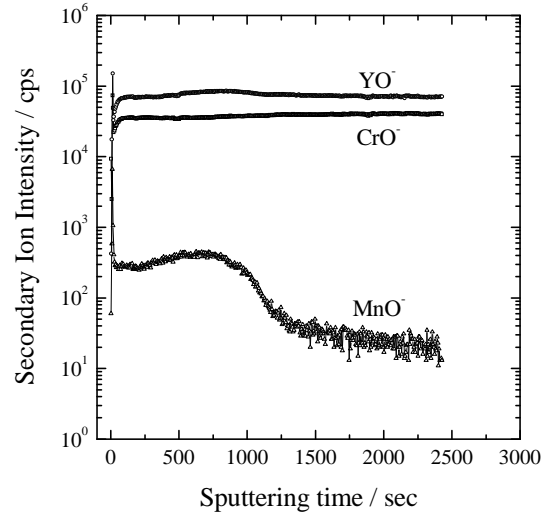
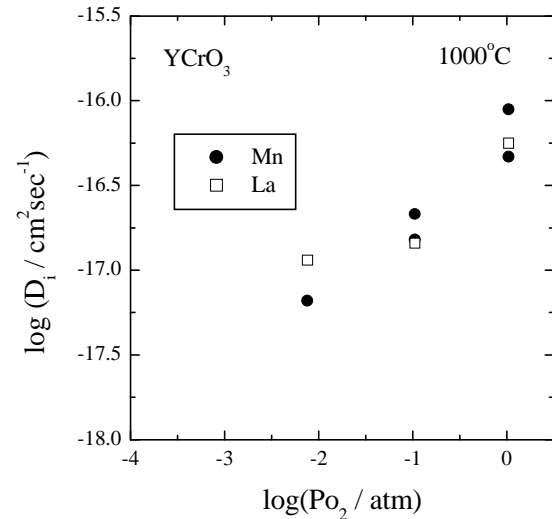


Fig. 1 Typical depth profile as measured by SIMS. The diffusion couple, $\text{Y}(\text{Cr}_{0.99}\text{Mn}_{0.01})\text{O}_3/\text{YCrO}_3$ was annealed



in $P_{\text{O}_2} = 1 \text{ atm}$ at 1000°C for 96h.

Fig. 2 Oxygen partial pressure dependence of the impurity diffusion coefficients at 1000°C . \bullet : D_{Mn} , \square : D_{La}